

## CLAIMS

What is claimed is:

1. A process for making a flexographic printing plate comprising:
  - 5 1) providing a photosensitive element comprising:  
at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer, and a photoinitiator, and at least one thermally removable layer disposed above the photopolymerizable layer, the thermally removable layer selected from the group consisting of
    - 10 (a) an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190 °C;
    - 15 (b) a layer of a composition comprising at least one binder and filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler, and
    - (c) a layer of particulate material having particle size of less than 23 micrometers;
  - 20 2) imagewise exposing the photopolymerizable layer to actinic radiation forming polymerized portions and unpolymerized portions; and
  - 3) thermally treating the element of step 2) by heating to a temperature sufficient to remove the thermally removable layer and to remove the unpolymerized portions of the photopolymerizable layer and form a relief.
- 25 2. The process of Claim 1 wherein the thermally removable layer selected from b) and c) is a release layer.
3. The process of Claim 1 wherein the thermally removable layer selected from b) and c) is an actinic radiation opaque layer.
- 30 4. The process of Claim 3 wherein the thermally removable layer b) further comprises (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different.
5. The process of Claim 3 wherein the thermally removable layer c) is radiation opaque and the particulate material can be a radiation opaque material, both a radiation opaque and infrared absorbing material, or combinations thereof.
- 35 6. The process of Claim 1 wherein the thermally removable layer completely covers the photopolymerizable layer.

7. The process of Claim 3 wherein the thermally removable layer is a mask layer having radiation opaque areas, further comprising the step of forming the mask layer imagewise from the thermally removable layer selected from a), b), or c), prior to step 2).

5 8. The process of Claim 7 wherein forming the mask comprises applying the thermally removable layer imagewise to the photopolymerizable layer.

9. The process of Claim 7 wherein forming the mask comprises applying as a complete covering layer the thermally removable layer to the photopolymerizable layer, and imagewise removing the thermally removable  
10 layer.

10. The process of Claim 7 wherein forming the mask comprises forming a carrier element having the thermally removable layer as the imagewise mask on a temporary support, laminating the carrier element to the photopolymerizable layer such that the thermally removable layer is disposed above a surface of the  
15 photopolymerizable layer opposite the support, and removing the temporary support.

11. The process of Claim 7 wherein forming the mask comprises delivering imagewise the thermally removable layer by ink jet methods.

12. The process of Claim 7 wherein the thermally removable layer is also  
20 sensitive to infrared radiation and forming the mask comprises:

forming a carrier element having the thermally removable layer on a substrate;

placing the carrier element onto the photopolymerizable layer such that the thermally removable layer is disposed above a surface of the  
25 photopolymerizable layer opposite the support;

imagewise exposing with infrared radiation the thermally removable layer to selectively change the adhesion balance of the thermally removable layer to substrate of the carrier element; and

removing the substrate with portions of the thermally removable layer.

30 13. The process of Claim 7 wherein the thermally removable layer is also sensitive to infrared radiation and forming the mask comprises:

placing a first element comprising at least the thermally removable layer on a substrate so that the thermally removable layer is in contact with or disposed above a surface of the photopolymerizable layer opposite the support;

35 imagewise exposing with infrared laser radiation the thermally removable layer to selectively transfer portions of the thermally removable layer to the photopolymerizable layer; and

separating the first element with portions of the thermally removable layer.

14. The process of Claim 7 wherein the thermally removable layer is also sensitive to infrared radiation and forming the mask comprises:

5           imagewise exposing with infrared laser radiation the thermally removable layer to selectively ablate portions of the thermally removable layer from the photopolymerizable layer.

15. The process of Claims 12, 13, and 14 wherein the infrared laser radiation is between 760 to 1064 nm.

10          16. The process of Claims 12, 13, and 14 further comprising impinging the infrared laser radiation on the thermally removable layer or through the support side of the photosensitive element.

17. The process of Claim 16 wherein the infrared laser radiation impinges the support side of the photosensitive element and further comprising locating a  
15       material capture element adjacent to the photosensitive element on a side opposite the support side to capture ablated portions of the thermally removable layer.

18. The process of Claim 3 wherein the imagewise exposing step 2) occurs in the presence of atmospheric oxygen.

19       The process of Claim 3 wherein the photosensitive element further  
20       comprises an additional layer between the thermally removable layer and the photopolymerizable layer, the additional layer being thermally removable at the treating temperature, and composed of materials selected from the group consisting of: polyamide, polyethylene oxide, polypropylene oxide, polyethylene wax, natural waxes, synthetic waxes, polypropylene, polyethylene, copolymers of  
25       styrene and acrylic polymers, copolymers of vinylpyrrolidone and vinyl acetate, copolymers of vinyl alcohol and vinyl acetate, polyacetate, copolymers of ethylene and acetate, and combinations thereof.

20. The process of Claim 1 wherein the photosensitive element further comprises a adhesion-modifying layer on the thermally removable layer, the  
30       adhesion-modifying layer being thermally removable at the treating temperature, and composed of materials selected from the group consisting of: polyamide, natural waxes, synthetic waxes, polyprpylene, polyethylene, copolymers of polyvinylpyrrolidone and vinyl acetate, amphoteric interpolymers, and combinations thereof.

35          21. The process of Claim 1 wherein the photosensitive element further comprises at least one more additional layer selected from the group consisting of: release layer, adhesion-modifying layer, barrier layer, and surface modifying

layer, wherein the at least one more additional layer is transparent to actinic radiation.

22. The process of Claim 1 wherein the binder of the thermally removable layer (a) is selected from the group consisting of: polyamides, polyethylene oxide,  
5 polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomers, cyclic rubber,  
10 copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, and combinations thereof.

23. The process of Claim 1 wherein the binder of the thermally removable layer (b) is selected from the group consisting of: polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose  
15 acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomer, copolymers of vinyl chloride and vinyl acetate, copolymers of styrene and butadiene, copolymers  
20 of styrene and isoprene, thermoplastic block copolymers of styrene and butadiene, thermoplastic block copolymers of styrene and isoprene, polyisobutylene, polybutadiene, polychloroprene, butyl rubber, nitrile rubber, thermoplastic polyurethane elastomer, cyclic rubbers, copolymers of vinylacetate and (acrylate or methacrylate), acrylonitrile-butadiene-styrene terpolymer, methacrylate-butadiene-styrene terpolymer, alkyl methacrylate polymer or copolymer,  
25 copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, polyvinyl alcohol, poly(meth)acrylic acids, metal alkali salts of poly(meth)acrylic acids, amphoteric interpolymers, hydroxyalkyl cellulose, cellulose acetate, nitrocellulose, polyimides, polyesters, polyphenylene ethers, polyacrylonitril, polystyrene, copolymers of styrene and methacrylic acid, polyvinyl chloride, polyesters, polyacrylamide, copolymers of imides and amides, polychlorotrifluoroethylene, ethylene and  
30 chlorotrifluoroethylene copolymer, polytetra fluoroethylene, copolymers of ethylene and tetrafluoroethylene copolymer, polyether ether ketone, polybenzimidazoles, copolymers of vinylidene fluoride and hexafluoropropylene, and combinations thereof..  
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24. The process of Claim 1 wherein the filler is selected from the group consisting of: mineral fillers, metallic fillers, metallic alloys, flame retardants, carbon black, graphite, pigments, and combinations thereof.

25. The process of Claim 24 wherein the filler has a particle size of less  
5 than 23 micrometers.

26. The process of Claim 1 wherein the particulate material is selected from the group consisting of: metals, metal alloys, carbon black, graphite, organic particles, inorganic particles, pigment particles, toner particles, mixtures of pigment particles, mixtures of toner particles, and mixtures of pigment and toner  
10 particles, and combinations thereof.

27. The process of Claim 1 wherein the at least one infrared absorbing material (i), the radiation opaque material (ii), the filler, and the particulate material in the thermally removable layer do not melt at the treating temperature.

28. The process of Claim 1 wherein the total amount of the at least one  
15 infrared absorbing material (i) and the radiation opaque material (ii) in the thermally removable layer (a) is less than 49 % by weight, based on the total weight of (i), (ii) and the binder of (a).

29. The process of Claim 1 wherein the thermally removable layer (b) is capable of microcracking to allow unexposed portions of the photopolymerizable  
20 layer to melt, soften, or flow at the treating temperature.

30. The process of Claim 1 wherein the thermally removable layer is (a).

31. The process of Claim 1 wherein the thermally removable layer is (b).

32. The process of Claim 1 wherein the thermally removable layer is (c).

33. The process of Claim 1 wherein the binder of the thermally removable  
25 layers (a) and (b) has a softening or melting temperature between 100°C and 190°C.

34. The process of Claim 33 wherein the binder of the thermally removable layer (b) has a softening or melting temperature greater than 190°C.

35. The process of Claim 1 wherein the binder of the thermally removable  
30 layer (a) is greater than 51% by weight, based on the total weight of (i), (ii) and the binder.

36. The process of Claim 1 further comprising contacting the photosensitive element of step 2) with an absorbent material during the treating step 3).

35 37. The process of Claim 36 further comprising applying pressure of 0.70 kilograms per square centimeter to about 7.03 kilograms per square centimeter during contacting the element and the absorbant material.

38. The process of Claim 36 further comprising applying pressure of 2.11 kilograms per square centimeter and about 4.92 kilograms per square centimeter during contacting the element and the absorbant material.

39. The process of Claim 1 wherein the thermal treating is heating the  
5 photosensitive element above about 40°C.

40. The process of Claim 39 wherein the thermal treating is heating the photosensitive element to between 100 and 200°C.

41. The process of Claim 36 wherein the heating of the photosensitive element and the contacting of the element with the absorbant material defines a  
10 cycle, and wherein the treating step comprises more than one cycle.

42. The process of Claim 41 wherein for each cycle the treating temperature and the pressure independently can be the same or different.

43. The process of Claim 2 wherein imagewise exposing further comprises:

15 placing a phototool imaged film on the thermally removable layer, exposing through the phototool with actinic radiation to selectively image the photopolymerizable layer, and removing the phototool prior to the step 3).

44. The process of Claim 2 wherein imagewise exposing further  
20 comprises:

placing at least one template having radiation opaque portion on the thermally removable layer,

25 exposing through the template with actinic radiation to selectively image the photopolymerizable layer, and removing the at least one template prior to step 3).

45. The process of Claim 3 further comprising ablating the actinic radiation opaque layer from the photopolymerizable layer, to form an *in situ* mask on the photopolymerizable layer prior to the imagewise exposing step 2).

46. The process of Claim 1 wherein at least 90 percent of the particulate  
30 (c) have the particle size of an equivalent spherical diameter of less than 23 micrometers.

47. The process of Claim 1 wherein at least 50 percent of the particulate (c) have the particle size of an equivalent spherical diameter of less than  
17 micrometers.

35 48. The process of Claim 1 wherein the thermally removable layer is present prior to the imagewise exposing step 2).

49. The process of Claim 3 wherein the thermally removable layer is radiation opaque and is present during the imagewise exposing step.

50. The process of Claim 1 wherein the at least one thermally removable layer is less than 50 microns thick.

51. A photosensitive element for use as a flexographic printing plate comprising:

5 at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer and a photoinitiator, wherein the photopolymerizable layer in an unexposed state is capable of melting, softening, or flowing at a treating temperature of at least 40°C, and

10 at least one thermally removable layer disposed above the photopolymerizable layer, wherein the thermally removable layer comprises at least one binder and a filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler.

52. The photosensitive element of Claim 51 wherein the thermally removable layer has a thickness less than 50 microns.

15 53. The photosensitive element of Claim 51 wherein the thermally removable is an actinic radiation opaque layer.

54. The photosensitive element of Claim 51 wherein the binder of the thermally removable layer is selected from the group consisting of: polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, 20 cellulose acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomer, copolymers of vinyl chloride and vinyl acetate, copolymers of styrene and 25 butadiene, copolymers of styrene and isoprene, thermoplastic block copolymers of styrene and butadiene, thermoplastic block copolymers of styrene and isoprene, polyisobutylene, polybutadiene, polychloroprene, butyl rubber, nitrile rubber, thermoplastic polyurethane elastomer, cyclic rubbers, copolymers of vinylacetate and (acrylate or methacrylate), acrylonitrile-butadiene-styrene terpolymer, 30 methacrylate-butadiene-styrene terpolymer, alkyl methacrylate polymer or copolymer, copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, polyvinyl alcohol, poly(meth)acrylic acids, metal alkali salts of poly(meth)acrylic acids, amphoteric interpolymers, hydroxyalkyl cellulose, cellulose acetate, nitrocellulose, 35 polyimides, polyesters, polyphenylene ethers, polyacrylonitril, polystyrene, copolymers of styrene and methacrylic acid, polyvinyl chloride, polyesters, polyacrylamide, copolymers of imides and amides, polychlorotrifluoroethylene, ethylene and chlorotrifluoroethylene copolymer, polytetra fluoroethylene,

copolymers of ethylene and tetrafluoroethylene copolymer, polyether ether ketone, polybenzimidazoles, copolymers of vinylidene fluoride and hexafluoropropylene, and combinations thereof.